PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Form PCT/IPEA/416
LU6149/CB		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP2004/014247	15.12.2004	19.12.2003

International Patent Classification (IPC) or national classification and IPC
C07F17/00, C08F10/00

Applicant
BASELL POLYOLEFINE GMBH et al.

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 6 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 5 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☒	Box No. VI	Certain documents cited
☒	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
27.09.2005	03.02.2006

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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/014247

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

   Description, Pages

   1-17 as originally filed

   Claims, Numbers

   1-10 received on 27.09.2005 with letter of 21.09.2005

   ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/EP2004/014247

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-10
	No:	Claims	-
Inventive step (IS)	Yes:	Claims	1-10
	No:	Claims	-
Industrial applicability (IA)	Yes:	Claims	1-10
	No:	Claims	-

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VI Certain documents cited

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

The following documents are mentioned in the International Search Report:

D1: BOLIG, ANDREW D. ET AL: "ansa-Zirconocene Ester Enolates: Synthesis, Structure, Reaction with Organo-Lewis Acids, and Application to Polymerization of Methacrylates" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 126, no. 15, 21 April 2004, pages 4897-4906

D2: BALBONI, DAVIDE ET AL: "Group 4 Dimethylmetallocenes: Improved Synthesis and Reactivity Studies" INORGANIC CHEMISTRY, vol. 40, no. 26, 17 December 2001, pages 6588-6597

D3: SOGA, KAZUO ET AL: "Polymerization of 1-olefins with bulky substituents catalyzed by an optically active metallocene catalyst" KOBUNSHI RONBUNSHU, vol. 54, no. 10, October 1997, pages 746-748

D4: HUTTENLOCH M E ET AL: "ansa-Metallocene derivatives XXXIX Biphenyl-bridged metallocene complexes of titanium, zirconium, and vanadium: syntheses, crystal structures and enantioseparation" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 541, no. 1-2, 15 August 1997, pages 219-232

D5: CHIN, BAIN ET AL: "Improved Procedure for the Preparation of Enantiomerically Pure Ethylenebis(tetrahydroindenyl)zirconium Derivatives" JOURNAL OF ORGANIC CHEMISTRY, vol. 62, no. 7, 4 April 1997, pages 2267-2268

D6: KAMINSKY W: "Stereospecific oligo- and polymerization with metallocene catalysts" MACROMOLECULAR SYMPOSIA, vol. 89, January 1995, pages 203-219

D7: KAMINSKY, WALTER ET AL: "Enantioselective oligomerization of alpha-olefins with chiral zirconocene/aluminoxane catalysts" ORGANIC SYNTHESIS VIA ORGANOMETALLICS (OSM4), PROCEEDINGS OF THE FOURTH SYMPOSIUM IN AACHEN, JULY 15 TO 18, 1992, 1993, pages 151-163

D8: CHIEN J C W ET AL: "Difference in stereoselective polymerization of 4-methyl-1-hexene by homogeneous and heterogeneous Ziegler-Natta catalysts" MAKROMOLEKULARE CHEMIE, RAPID COMMUNICATIONS, vol. 13, no. 11, 1 November 1992, pages 479-484

D9: KAMINSKY, WALTER ET AL: "Asymmetric oligomerization of propene and 1-butene with a zirconocene-aluminoxane catalyst" ANGEWANDTE CHEMIE, INTERNATIONAL EDITION, vol. 28, no. 9, 1989, pages 1216-1218

D10: SCHAEFER, ANDREA ET AL: "ansa-Metallocene derivatives. XII. Diastereomeric derivatization and enantiomer separation of ethylenebis(tetrahydroindenyl)titanium and zirconium dichlorides" JOURNAL OF ORGANOMETALLIC CHEMISTRY, vol. 328, no. 1-2, 14 July 1987, pages 87-99

D11: WO 2004/037840 A (BASELL POLYOLEFINE GMBH) 6 May 2004

D12: WO 2004/037834 A (BASELL POLYOLEFINE GMBH) 6 May 2004

D13: US-B1-6 548 441 (MCDANIEL MAX P ET AL) 15 April 2003

Re Item V.

The subject-matter of claims 9 and 10 as originally filed was not found to be novel on the following grounds:

the way in which substituent R^3 was originally defined (R^3 is a bulky organic radical which has at least 3 carbon atoms, is bound to the oxygen atom via a non-aromatic carbon or silicon atom and may be substituted by halogen atoms or further organic radicals having from 1 to 20 carbon atoms and may also contain heteroatoms selected from the group

consisting of Si, N, P, O and S) meant that documents D2-D10 disclosed compounds falling under the scope of compounds of formula (I):
D10 - Table 1; D9 refers to (S)-[1,1'-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium bis(O-acetyl-(R)-mandelate) and its use in the asymmetric oligomerisation of propene and 1-butene; the same compound is mentioned in D8 but this time it is used in the polymerisation of 4-methyl-1-hexene; the same compound is again employed in D7, this time in the oligomerisation of propene; the compound is yet again mentioned in D6, employed this time to oligomerise 1-butene, 1-pentene and propene; D5, compounds 1c and 2c; D4, compound 14a; D3, a further document mentioning the (S)-ethylenebis(tetrahydroindenyl)]zirconium bis(O-acetyl-(R)-mandelate) using in combination with MAO in the polymerisation of 1-olefins with bulky substituents; and D2 (cf. page 6596, column 2, lines 4ff. disclosing the compound meso-$C_2H_4(4,7\text{-}Me_2Ind)_2ZrMe(O\text{-}t\text{-}Bu)$).

By restricting the definitions of claim 9 to those according to original claim 4, novelty for claims 9 and 10 can be acknowledged.

Additionally there is no teaching in the prior art of the compounds having formula (I) having the specific substituents as given in amended claim 9. Claims 9 and 10 can therefore be seen to be based upon an inventive step.

The subject-matter of claims 1-8 is seen to meet the requirements of Article 33(2) PCT as the prior art does not divulge a process for preparing the metallocenes of original claim 9 in such a manner, nor the intermediates involved in said preparation method.

The subject-matter of claims 1-8 is seen to also meet the requirements of Article 33(3) PCT in that the prior art does not suggest the preparation methods or intermediates addressed in these claims.

Re Item VI.

Documents D1, D11 and D12 are documents published in the priority interval of the present application and as such are not to be regarded as prior art according to Rule 64.3 PCT.

D11 and D12 are recent applications from the applicant. D11 interestingly discloses a preparation process similar to that presently claimed but with different end products. D1 discusses ansa-zirconocene enolates falling under the scope of original claim 9 but not under the scope of amended claim 9, the compounds of D1 being prepared differently to the method of claim 1.

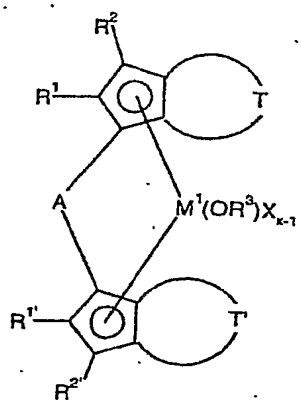
Re Item VII.

The article cited as prior art on page 1, line 32 does not exist - the applicant has identified the correct citation as being Organometallics, 1997, 16(4), pages 713-715. The correction needs to be made to the citation.

Additionally the description requires amendments to bring it into line with the amended claims.

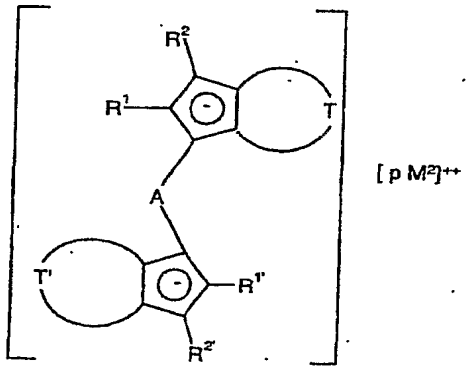
We claim:

1. A process for the meso-selective preparation of ansa-metallocene complexes of the formula (I),



(I)

which comprises reacting a ligand starting compound of the formula (II)



(II)

with a transition metal compound of the formula (III)

$$(LB)_yM^1(OR^3)X_{x+1} \qquad (III)$$

where

R^1, $R^{1'}$ are identical or different and are each hydrogen or an organic radical having from 1 to 40 carbon atoms,

R^2, $R^{2'}$ are identical or different and are each hydrogen or an organic radical having from 1 to 40 carbon atoms,

R^3 is a bulky organic radical which has at least 3 carbon atoms, is bound to the oxygen atom via a nonaromatic carbon or silicon atom and may be substituted by halogen atoms or further organic radicals having from 1 to 20 carbon atoms and may also contain heteroatoms selected from the group consisting of Si, N, P, O and S,

T, T' are identical or different and are each a divalent organic group which has from 1 to 40 carbon atoms and together with the cyclopentadienyl ring forms at least one further saturated or unsaturated, substituted or unsubstituted ring system having a ring size of from 5 to 12 atoms, where T and T' may contain the heteroatoms Si, Ge, N, P, As, Sb, O, S, Se or Te within the ring system fused to the cyclopentadienyl ring,

A is a bridge consisting of a divalent atom or a divalent group,

M^1 is an element of group 3, 4, 5 or 6 of the Periodic Table of the Elements or the lanthanides,

the radicals X are identical or different and are each an organic or inorganic radical which is able to be replaced by a cyclopentadienyl anion,

x is a natural number from 1 to 4,

M^2 is an alkali metal, an alkaline earth metal or a magnesium monohalide fragment,

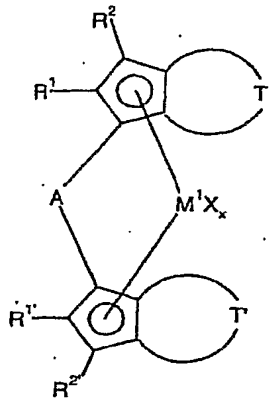
p is 1 in the case of doubly positively charged metal ions or 2 in the case of singly positively charged metal ions or metal ion fragments,

LB is an uncharged Lewis base ligand,

and

y is a natural number from 0 to 6.

2. A process as claimed in claim 1, wherein the metallocene complex of the formula (I) is converted into an ansa-metallocene complex of the formula (IV)



(IV)

where

the variables and indices have the same meanings as in the formula (I), by reaction with suitable elimination reagents in a subsequent reaction step.

3. A process as claimed in claim 1 or 2, wherein

R^1, $R^{1'}$ are identical or different and are each C_1-C_{10}-alkyl,

R^2, $R^{2'}$ are each hydrogen,

T, T' are identical or different and are each an unsubstituted 1,3-butadiene-1,4-diyl group or a 1,3-butadiene-1,4-diyl group substituted by from 1 to 4 radicals R^4, where R^4 can be identical or different and are organic radicals having from 1 to 40 carbon atoms,

A is ethylene, substituted ethylene or substituted silylene,

and the variables R^3, M^1, X, M^2 and LB and also the indices x, p and y are as defined in claim 1.

4. A process as claimed in any of claims 1 to 3, wherein

R^3 is an alkyl radical which is branched in the α position and has from 4 to 40 carbon atoms and may be substituted by halogen atoms or organic radicals having from 1 to 10 carbon atoms,

M^1 is Ti, Zr or Hf,

X is halogen,

x is 2,

LB is a cyclic or acyclic ether or diether,

and

y is 1 or 2.

5. A process as claimed in any of claims 1 to 4, wherein

M^2 is Li, Na, K, MgCl, MgBr, MgI or Mg.

6. The use of a transition metal compound of the formula (III)

$$(LB)_yM^1(OR^3)X_{x+1} \qquad (III)$$

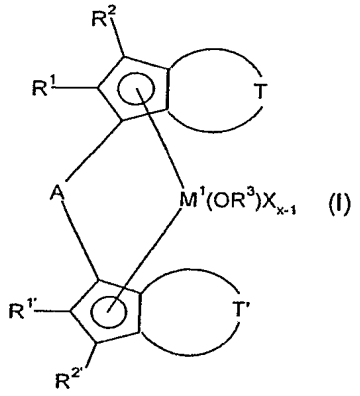
for preparing ansa-metallocene complexes.

7. A transition metal compound of the formula (III)

$$(LB)_yM^1(OR^3)X_{x+1} \qquad (III)$$

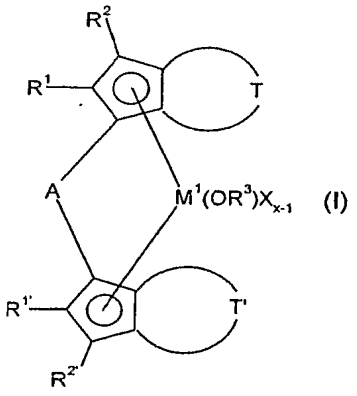
where the variables and indices are as defined in claim 1 or claim 4.

8. The use of a metallocene complex of the formula (I) as set forth in claim 1



as intermediate for preparing ansa-metallocene complexes of the formula (IV), where the variables and indices are as defined in any of claims 1, 3 and 4.

9. An ansa-metallocene complex of the formula (I) as set forth in claim 1



where
R^1, $R^{1'}$, R^2, $R^{2'}$, T, T' and A are as defined in claim 1 and
where
R^3, M^1, X and x are as defined in claim 4.

10. The use of an ansa-metallocene complex of the formula (I) as claimed in claim 9 as constituent of a catalyst system for the polymerization of olefins.